Development of Scanning X-ray Microscopes for Materials Science Spectromicroscopy at the Advanced Light Source

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INTRODUCTION

NEXAFS and XPS spectroscopies are applied in a pair of scanning zone-plate microscopes which have become operational at undulator beamline 7.0 at the ALS. Figure 1 shows this facility. The count rates in these microscopes are about ten times higher than previously available.

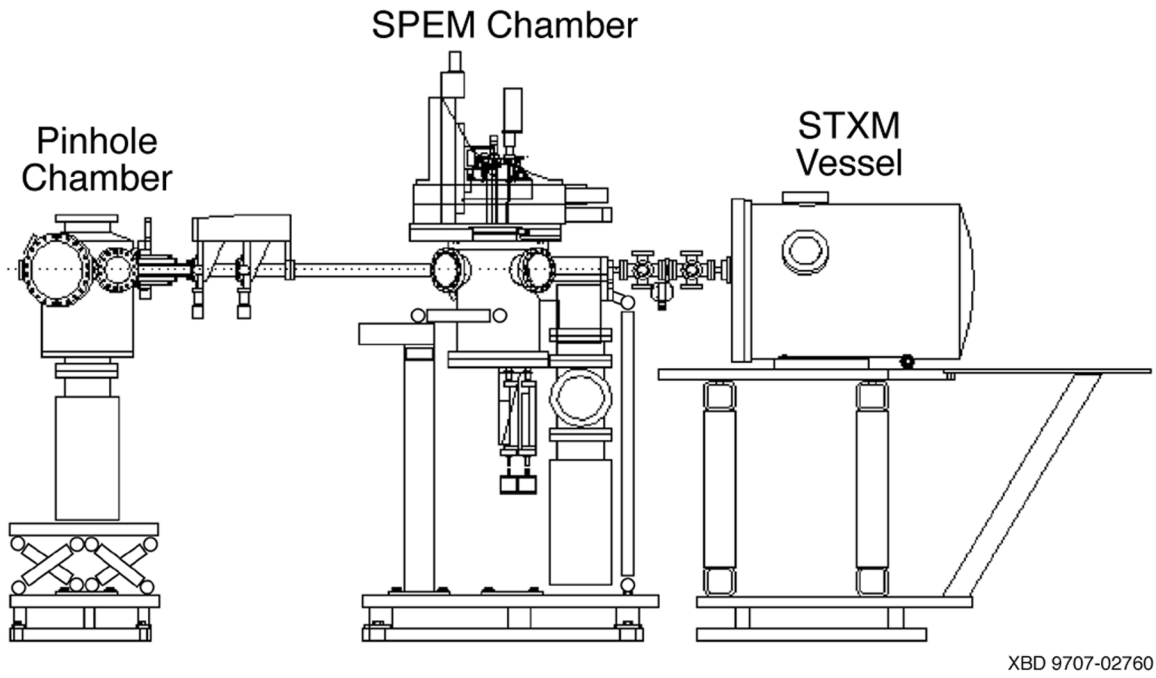

Figure 1. The tandem layout of the two microscopes. The upstream microscope is a UHV Scanning PhotoElectron Microscope (SPEM). The photon beam passes through the SPEM chamber to STXM, which is the last item in the beamline.

THE SCANNING TRANSMISSION X-RAY MICROSCOPE (STXM)

Figure 2 illustrates the zone plate scheme employed in STXM. The lens is outside a Si_3N_4 vacuum window 160nm thick. We are presently using lenses with 80nm outer zone width, and a corresponding diffraction limit to the spatial resolution of about 100nm. Images made of fractured

thin windows (100nm Si_3N_4) show blurring consistent with an x-ray spot size of 150nm FWHM. The order sorting aperture (OSA) is precisely positioned on the optical axis (+/-2 microns) to allow only the first order diffracted focus to reach the sample. This aperture is a photo-sensitive element which generates a signal (a few pA) proportional to the illumination intensity for spectral normalization against the effects of low frequency (<10Hz) beam motion in the beamline, which cannot be averaged over the counting interval (few hundred milliseconds). We have measured 2 x 10^7 photons/second with a spectral width 1/3000 in the zone plate first order focus spot at 300eV, with the storage ring running at 1.5 GeV, 400mA. At higher photon energies the intensity increases, as the windows become more transparent, until the beamline output decreases above 500eV. Images are typically acquired with a counting time of 10ms per pixel. NEXAFS spectra are acquired with a counting time of several hundred ms per energy point. Coordinated undulator and monochromator moves take about 250ms to complete, during which time a fast mechanical shutter closes to protect radiation sensitive samples from unnecessary exposure.

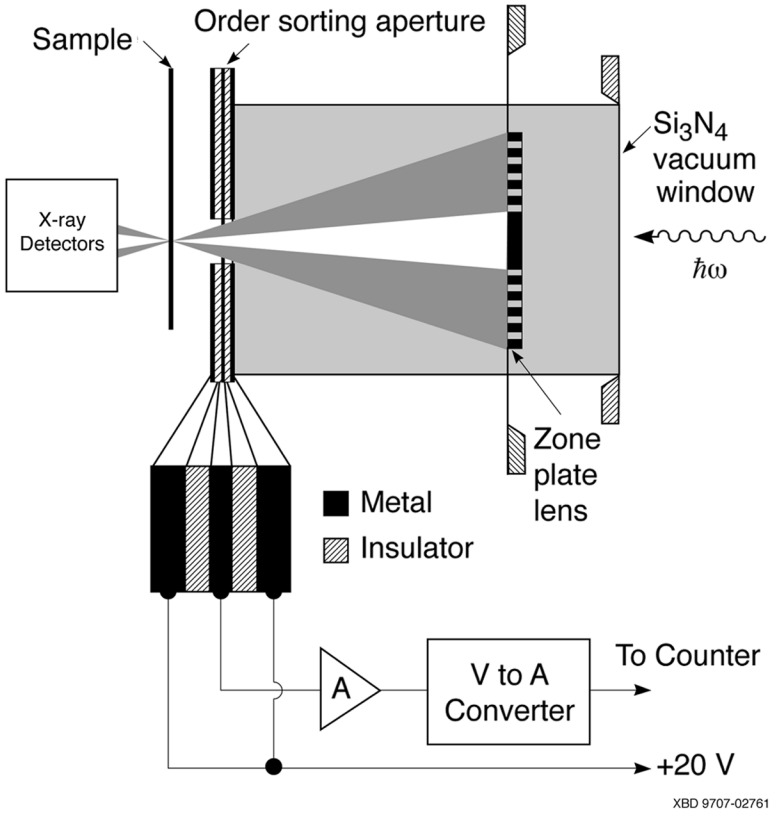

Figure 2. Schematic arrangement of the windows, lens, order sorting aperture (OSA), the sample and the detector in STXM.

The transmission geometry is the most efficient use of photons for an absorption spectrum, well suited to radiation sensitive organic samples.

Measurements in transmission are bulk sensitive, so that surface contamination is not a concern. This allows the operation of the microscope at atmospheric pressure, in air or helium, with hydrated samples for problems in environmental science.

The most difficult mechanism involved in this microscope is the flexure which translates the zone plate longitudinally through 0.5mm to remain in focus as the photon energy is changed during a NEXAFS scan. This mechanism inevitably has some unwanted sideways run-out (about 0.4 microns) which is reproducible and compensated by programmed sideways motion of the sample during the spectral scan. The resulting lock-in (0.2 microns) allows spectra to be measured with some confidence on features uniform over regions as small as 0.5 microns. We are presently making a transition to finer zone plates (spatial resolution improved by a factor of 2) with shorter focal lengths (by a factor of 4) so that the spatial resolution will be improved and this difficult translation will be smaller.

Photons are detected in transmission by one of two detectors.
1) An analog silicon photo-diode (from International Radiation Detectors, Torrance, CA90505, USA) for full intensity measurements. This detector is essentially 100% efficient above 100eV except for a thin oxide layer. It is typically used with a 10ms amplifier time constant.
2) A photo-multiplier tube collecting visible light from a phosphor (P43) behind the sample. This scheme is under development but shows overall x-ray counting efficiency of 25% and is linear beyond 1MHz counting rate.

Figure 3 shows a case study illustrating the STXM capabilities. In this case the polarization/orientation sensitivity is explored at the K edge of three atoms in the molecule; carbon, oxygen and nitrogen. The latter two measurements require a pure helium environment to remove atmospheric absorption effects.

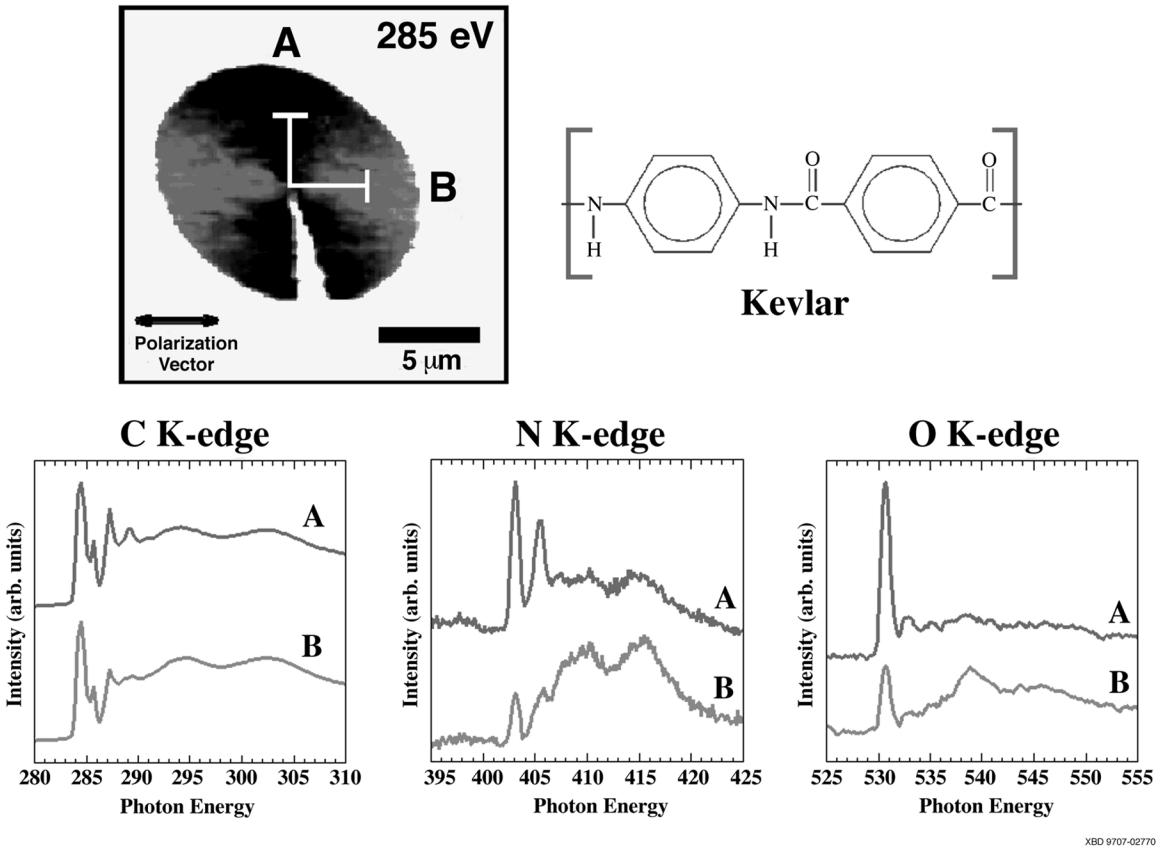

Figure 3. A sectioned Kevlar fiber measured in STXM. Absorption spectra are measured at points A and B, showing the dependence on the angle between the photon polarization vector (horizontal) and the radially oriented polymer chains. Spectra are shown for each of the main atomic species present. The polarization contrast reverses between the pi and sigma orbital peaks.

THE SCANNING PHOTO-EMISSION MICROSCOPE (SPEM)

Figure 4 illustrates the zone plate scheme employed in SPEM. Here the sample is stationary during imaging and the zone plate is rastered in the illumination field to carry the focused spot across the sample surface. The illumination is of the order of 1mm diameter and the raster range is 80x80 microns. The electron spectrometer can view the entire range of the image area and collects photo-electrons at 60 degrees from the sample normal. The OSA is within 0.5mm of the sample surface, and the zone plate assembly is cut back on one side to allow a line of sight for the spectrometer. NEXAFS capability is included by means of a flexure to carry the zone plate 0.5mm longitudinally

to retain the focus condition as the photon energy changes. The OSA moves away from its optimum longitudinal position during a NEXAFS scan but not so far as to intercept the first order light.

The OSA is fixed to the zone plate, with the focal length built in to the assembly. Different photon energies require different zone-plate/OSA combinations with different built-in focal lengths (e.g. 620eV for survey spectra including oxygen 1s photoelectrons, 270eV to 310eV for carbon K edge NEXAFS measurements). Five zone plates will be mounted together on a monolithic array with precisely parallel optical axes (to +/-1mrad), interchangeable under computer control. So far we have operated the microscope with three zone-plate/OSAs aligned in this way. SPEM allows us to perform quantitative XPS measurements of atomic concentration and core level chemical shifts over regions of the sample surface as small as the spatial resolution of the zone plate lens (currently x-ray spots smaller than 0.3 microns have been achieved). The zone plate array can be lowered out of the beam and the sample surface can be observed with the same video system, allowing visible fiducial marks on the sample to be used to position the region of interest within the 100x100 micron range of the scan stage. XPS spectra are measured with typical photo-peak count-rates of 70,000 counts/second (Au 4f at 420eV photon energy).

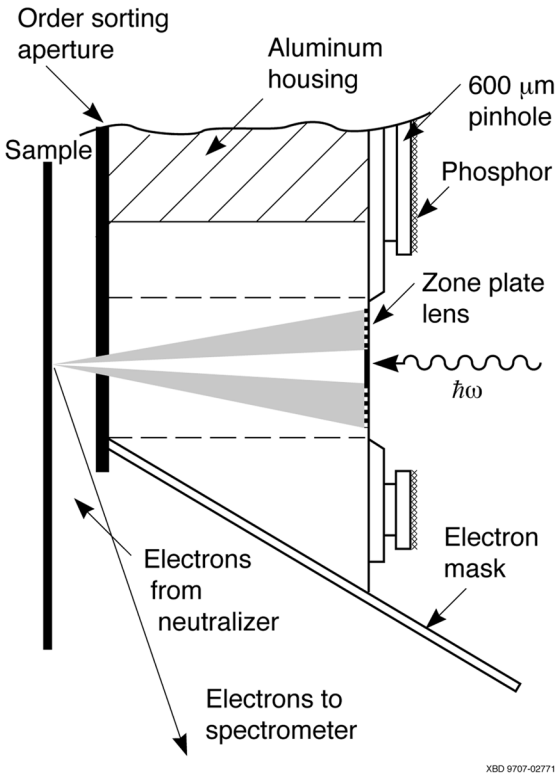

Figure 4. Schematic arrangement of the lens, order sorting aperture (OSA), the sample and the spectrometer in SPEM.

Sample charging is partially neutralized by the proximity of the zone plate assembly to the sample surface (which serves as a source of low energy electrons) and by an electron flood gun. Remaining charging shifts are corrected relative to the photo-emission peaks of contaminant carbon or to a Fermi edge. Sample sputtering and annealing is provided in a preparation chamber adjacent to the microscope chamber. The instrument operates at 5×10^{-10} Torr.

Figure 5 shows a SPEM case study in which an Al/Ti melt has been allowed to solidify on a graphite substrate. The image of the polished section shows the aluminum metal, precipitates of Al_3Ti alloy and the graphite interface, with carbide formation. Different core level chemical shifts are observed from the Al, the Al_3Ti alloy and the carbide region. Topography is visible in the image because of the sideways collection of electrons. The harder alloy precipitates are proud of the metal surface after polishing. In this case sputtering has removed the adventitious carbon contamination but the surface is still oxidized.

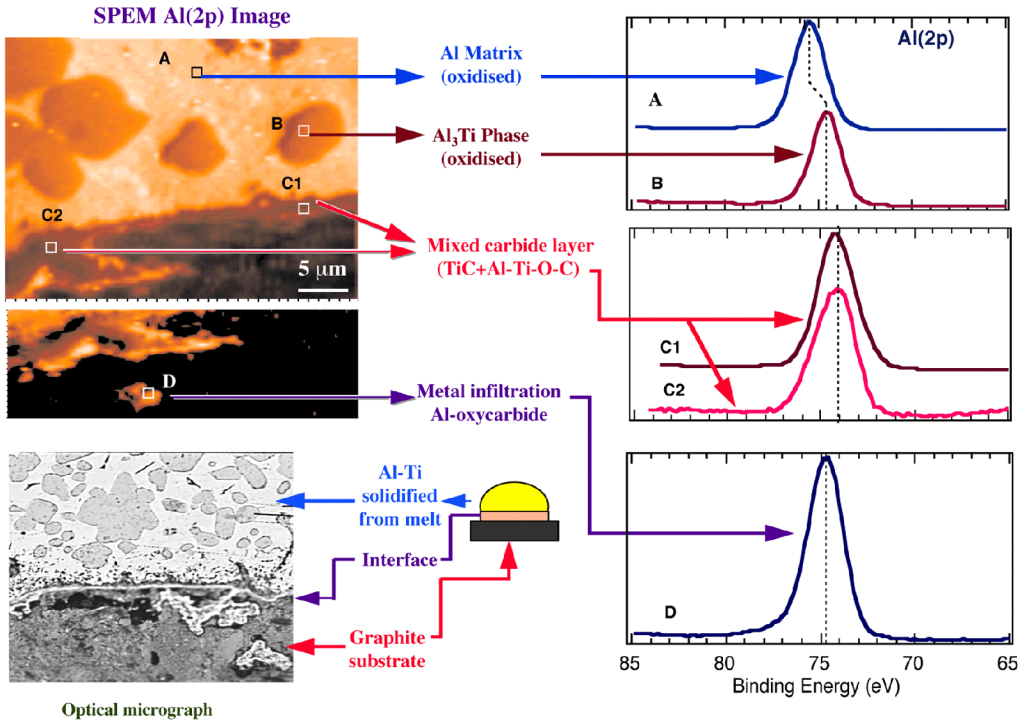

Figure 5. SPEM images and Al 2p XPS spectra from a metallurgical study of Al/Ti melt interactions with solid graphite. Early results provide quantitative chemical shifts and stoichiometry of alloy precipitates and carbide formation at the interface.

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